Chemistry 2710 Spring 2003 Test 2

Marks: 44

Aids allowed: Calculator. One $8\frac{1}{2} \times 11$-inch piece of paper containing any information you need. No other printed materials (e.g. periodic tables, calculator manuals) are allowed.

Instructions: Answer all questions in the booklets provided.

Note: Clarity may be considered in evaluating your answers.

1. The following rate constants have been measured for the reaction $\mathrm{HOBr_{(aq)} + Br^-_{(aq)} + H^+_{(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_{2(aq)} + H_2O_{(l)}}$:

$$\begin{aligned} k_1 &= 1.6 \times 10^{10}\,\mathrm{L^2 mol^{-2} s^{-1}} \\ k_{-1} &= 110\,\mathrm{s^{-1}} \end{aligned}$$

   (Because water is present in great excess and its concentration doesn't vary during the experiment, the reverse reaction behaves like a first-order reaction.) From thermodynamics, we can calculate that the equilibrium constant is $1.7 \times 10^8\,\mathrm{L^2/mol^2}$. Are the rate constant measurements consistent with thermodynamics? [5 marks]

2. The reaction $\mathrm{2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}}$ is thought to be elementary.[1] Suppose that there is initially no NOCl present, and that the initial concentrations of NO and of $\mathrm{Cl_2}$ have no particular relationship. Work out the integrated rate law for this reaction, right up to the step of taking the integral. *Do not evaluate the integral.* In other words, leave your answer in the form $t = \int_a^b f(z)\,dz$ (where z, $f(z)$, a and b have been replaced by appropriate expressions, of course). [10 marks]

[1] Yes, it's another one of those supposedly rare termolecular gas-phase elementary reactions. There's nothing a physical chemist likes better than a good exception, so there's a disproportionate amount of information available on termolecular reactions.

3. Consider the mechanism

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{B},$$
$$\mathrm{B} \xrightarrow{k_2} \mathrm{C}.$$

(a) Write down mass-action rate equations for all three species. [3 marks]

(b) Determine the overall reaction. [2 marks]

(c) Suppose that the second step of the reaction is slow. Obtain an approximate rate law which only involves the concentration of A. [6 marks]

(d) Write down the integrated rate law corresponding to the rate law you obtained in part c. Discuss briefly how you would use this integrated rate law to determine the rate constants, and what information you could or could not obtain by this method. Be clear about what type of experiment(s) you would carry out and how you would treat the data. [8 marks]

(e) Sketch the trajectories for this mechanism in the (a, b) phase plane. Is your sketch consistent with the rate law you obtained in part c? Explain briefly. [10 marks]

Hint: To plot the nullclines, you will find it convenient to solve for a as a function of b rather than the other way around.